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Are models of catalytic removal of O_3 by HO_x accurate? Constraints from in situ measurements of the OH to HO_2 ratio

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Abstract. Measurements of the ratio OH/HO_2, NO, O_3, ClO, and BrO were obtained at altitudes from 15–20 km and latitudes from 15–60°N. A method is presented for interpreting these simultaneous *in situ* observations that constrains the rates of chemical transformations that 1) are responsible for over half the ozone removal rate in the lower stratosphere via reactions of HO_2 and 2) control the abundance of HO_2 through coupling to nitrogen and halogen radicals. The results show our understanding of the chemical reactions controlling the partitioning of OH and HO_2 is complete and accurate and that the potential effects of "missing chemistry" are strictly constrained in the region of the atmosphere encompassed by the observations. The analysis demonstrates that the sensitivity of the ratio OH/HO_2 to changes in NO is described to within 12% by current models. This reduces by more than a factor of 2 the effect of uncertainty in the coupling of hydrogen and nitrogen radicals on the analysis of the potential effects of perturbations to odd nitrogen in the lower stratosphere.

Introduction

In situ measurements from the Stratospheric Photochemistry, Aerosols, and Dynamics Expedition (SPADE) provide the first simultaneous set of measurements of the radicals (HO_2, ClO, BrO, and NO_2) responsible for catalytic destruction of ozone. *Wennberg et al.* [1994a] used the SPADE observations, along with rate constants from laboratory measurements, to empirically determine the rate of the chemical destruction of ozone at altitudes from 15–20 km and latitudes from 15–60°N during May 1993. Throughout this region of the atmosphere, the measurements show that HO_x ($HO_x \equiv OH+HO_2+H$) catalysis:

$$OH + O_3 \rightarrow HO_2 + O_2 \quad (R_1)$$
$$HO_2 + O_3 \rightarrow OH + O_2 + O_2 \quad (R_2)$$
$$\text{Net: } 2O_3 \rightarrow 3O_2$$

constituted 30–50% of the total odd-oxygen loss. The coupled HO_2/ClO and HO_2/BrO catalytic cycles:

$$HO_2 + XO \rightarrow HOX + O_2 \quad (R_{3a,b})$$
$$HOX + h\nu \rightarrow OH + X \quad (R_{4a,b})$$
$$OH + O_3 \rightarrow HO_2 + O_2 \quad (R_1)$$
$$X + O_3 \rightarrow XO + O_2 \quad (R_{5a,b})$$
$$\text{Net: } 2O_3 + h\nu \rightarrow 3O_2$$

[X≡Cl (a) or Br (b)] were responsible for one half of the halogen-controlled ozone removal and 15% of the total odd-oxygen loss rates. Taken together, the three reactions involving HO_2 (R_1, R_{3a}, and R_{3b}) were rate limiting in cycles responsible for more than half of the total photochemical ozone removal in the northern hemisphere lower stratosphere during May 1993.

It is only recently that models [e.g., *Rodriguez et al.* 1991] have predicted that catalysis by HO_2, ClO, and BrO radicals control the rate of chemical ozone removal in the lower stratosphere and consequently that catalysis by odd-nitrogen radicals (NO_x) is considerably less important. The inclusion of efficient hydrolysis of N_2O_5 in recent models is responsible for reordering the importance of the catalytic cycles. *Fahey et al.* [1993] confirmed the model predictions of slow NO_x catalysis by direct *in situ* measurement of the NO radical and total odd-nitrogen concentrations. The SPADE results are the first to directly demonstrate the importance of the hydrogen radicals by simultaneous measurement of HO_2, ClO, BrO, and NO_2.

Our new appreciation of the prominence of HO_2 underscores the need for quantitative description of its concentration and kinetics and its response to natural and/or anthropogenic perturbations. We present precise (±4%) and accurate (±13%) *in situ* stratospheric measurements of the ratio OH/HO_2. Measurements of the hydroxyl radical obtained during SPADE are described by *Wennberg et al.* [1994a]. We find that the OH mixing ratio is nearly independent of the concentration of NO, NO_2, total odd-nitrogen (NO_y), O_3, or H_2O; it is determined almost solely by the solar flux. In contrast, HO_2 is more variable, driven directly by the atmospheric concentrations of O_3, NO, ClO, etc. Figure 1 shows the measurements of OH/HO_2 vs. latitude from the flights of May 1 and 3, 1993. A calculation of the ratio (described below) is shown as a solid line.

Previous attempts to interpret measurements of OH/HO_2 [*Wennberg et al.*, 1990, *Park and Carli*, 1991] were hampered by the lack of simultaneous NO measurements and by the limited data set obtained by the balloon-borne experiments. Despite these difficulties, *Wennberg et al.* showed that their measurements could be modeled using a small reaction set and an estimate of the NO profile to within the combined uncertainties of the measurements and of the reaction rates. The new measurements of OH/HO_2 are more extensive and are obtained simultaneously with measurements of O_3, NO, ClO, and BrO. Concentrations of the observed chemical species span a wide range, rigorously testing models of HO_x partitioning. The

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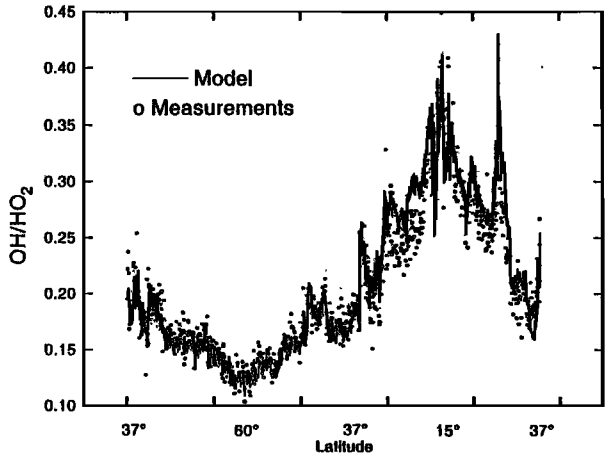

Figure 1. Measured (o) and modeled (—) OH/HO_2 vs. latitude.

results show our understanding of the chemical reactions controlling the partitioning of OH and HO_2 is complete and accurate. In addition, we constrain the absolute rates and the ratios of the rates of R_1, R_2, R_3, and the competing reaction

$$HO_2 + NO \rightarrow OH + NO_2 \qquad (R_6)$$

at temperatures near 210 K. Constraints on these rates represent a substantial reduction in the uncertainty associated with models that employ them 1) to calculate the rate of ozone removal by reactions involving HO_2 and 2) to describe the response of HO_x to changes in NO (e.g., from the injection of aircraft exhaust or of volcanic aerosol precursors into the stratosphere).

The Data Set

The instrumentation used to measure OH and HO_2 from the ER-2 is described by *Wennberg et al.* [1994b]. Briefly, OH is measured by laser induced fluorescence (LIF) at mixing ratios as small as 0.01 ppt. HO_2 is measured by chemical conversion to OH by reaction with NO added as a reagent, as in R_6, followed by LIF detection of OH. The chemical titration of HO_2 is complicated by the three-body reaction of OH with NO:

$$OH + NO + M \rightarrow HONO + M \qquad (R_7)$$

Data for both OH and HO_2 are reported every 25 sec. Variable concentrations of NO are used during each HO_2 measurement. HO_2 is then determined from a fit of the OH detected to a calculation including R_6 and R_7, the mass flow of NO, and the measured velocity of the air within the instrument. The large dynamic range afforded by scanning [NO] and the flow velocity allows direct demonstration of the rapid mixing of NO into the flow and the rate of OH formation and removal during flight.

The uncertainty in OH/HO_2 is independent of the accuracy of the instrument with respect to OH (20%). (All uncertainties used here are 1σ confidence intervals; "absolute," "systematic," and "accuracy" refer to errors and uncertainties that are not randomly distributed.) The accuracy depends only on the uncertainty in the HO_2 to OH conversion efficiency. In-flight measurements of the relative rates of R_6 and R_7 show that the conversion efficiency is known to within 13%. The precision of the measurements is ~4%, due both to shot noise in the photon counting and limitations of the HO_2 titration procedure.

The SPADE ER-2 payload included instruments that measure most of the chemical species thought to control the ratio of OH to HO_2; these include O_3, NO, ClO, and BrO. The full data set has been made available [*Hathaway et al.*, 1994]. The limited accuracy and precision of these measurements are a possible source of uncertainty in the calculated ratio of OH to HO_2. The ozone measurement is accurate to 2% and precise to ~1%. These are much smaller than the uncertainty in the rates of the HO_x+O_3 reactions and the precision of the OH/HO_2 measurements. The accuracy in the NO measurement is 10%; the precision is typically 3%. The ClO measurement is accurate to 15%. BrO was not measured on all the flights and is only available at a few points per flight. We assume the BrO that would have been observed simultaneously with the other measurements to be 45% of the inorganic bromine in that air parcel [*Wennberg et al.*, 1994a]. We estimate that BrO is uncertain to a factor of 1.5.

CO was not accurately measured on the ER-2 during SPADE. We estimate CO based on data reported by *Murphy et al.* [1993] describing the correlation of CO with ozone in the tropics and from CO and O_3 data taken at mid latitudes [*S.E. Strahan* and *M.H. Proffitt*, private communication]. We use the tracer N_2O as a surrogate for O_3 because O_3 was a poor tracer during the Spring 1993. The relation used is: CO (ppb) = -31 log(310-N_2O (ppb))+70, or CO = 10 ppb, whichever is greater. Uncertainty in the CO estimate is substantial so the exact details of the O_3-N_2O relations are not important. While it is unlikely that CO is much less than our estimate, CO might be as much as four times higher [see *Elkins et al.* in *Hathaway et al.*, 1994].

The data employed in our analysis include the SPADE measurements collected at air densities less than 3×10^{18} mol/cm^3, [O_3] greater than 1.5×10^{12} mol/cm^3, the ratio OH/HO_2 greater than 0.05, and solar zenith angles less than 85°. These constraints insure that the data were collected in the stratosphere and that measurements of the radicals are at concentrations well above the detection limits of the instruments. We also exclude all measurements where a doubling of CO would cause more than an 8% change in the modeled ratio, insuring that the lack of direct experimental knowledge of CO concentrations does not affect our conclusions. More than 70% of the measurements meet these criteria. Data reported at high rates (e.g., NO and O_3, 1 Hz) were averaged for 10 sec symmetrically about the OH/HO_2 measurement. For measurements reported less frequently, data within 10 sec of the OH/HO_2 measurement were used. The measurements of OH/HO_2 were made over a wide range of [O_3], $0.4–4\times10^{12}$ mol/cm^3, and [NO], $3–11\times10^8$ mol/cm^3. More importantly, large gradients in [NO] were sampled at constant values of [O_3] and vice versa.

Analysis

Production and loss of OH and HO_2 in the lower stratosphere occur via 100 or so photochemical reactions. The interconversion of OH and HO_2 occurs roughly 10 times faster (τ=10 sec) than the sum of processes contributing to net increase or decrease of HO_x (τ=100 sec). Accordingly, we assume OH and HO_2 are in photochemical steady state (an approximation the measurements show to be good to better than 4%, since at no time is the ratio correlated with the net production or loss of HO_x). The HO_x catalytic reactions (R_1 and R_2) and the reaction of HO_2 with NO (R_6) describe the partitioning quite well throughout the region of the stratosphere sampled by the ER-2 during SPADE. A more complete model nearly quantitatively reproduces the measured OH to HO_2 ratio (Fig. 1):

$$\frac{[OH]}{[HO_2]} = \frac{k_6[NO] + k_2[O_3] + k_{3a}[ClO] + k_{3b}[BrO]}{k_1[O_3] + k_8[CO]} \qquad (1)$$

Equation 1 includes all the reactions thought to be important (> 5%) in the interconversion of OH and HO_2. The reaction:

$$OH + CO \rightarrow H + CO_2 \qquad (R_8)$$

is followed instantly by reaction of H and O_2 to form HO_2. We also assume that HOCl and HOBr are in photochemical steady state. The HOCl and HOBr formed in R_{3a} and R_{3b} are then a direct source of OH. Rate constants used in the calculation [*DeMore, et al.*, 1992, hereafter JPL'92] are given in Table 1.

Agreement between Eq. 1 and the measurements shown in Fig. 1 is striking. Recall that the absolute uncertainty in the measurement of OH/HO_2 is 13% and that the accuracy in the NO measurement is 10%. The rate constants are considered by JPL'92 to be even less well known. Fig. 2 shows measurements of OH/HO_2 plotted vs. $[O_3]$. These data were collected at [NO] $=7.5\pm0.1\times10^8$ mol/cm^3 and thus define the specific response of OH/HO_2 to changes in O_3 alone. The dotted line shows Eq. 1 when all rates are fixed at JPL'92 values. Solid and dashed lines describe the ratio when the rates of R_1 (dashed) or R_2 (solid) are assumed to proceed at the JPL'92 1σ uncertainty at 210 K. Similarly, Fig. 3 shows the ratio vs. [NO] at nearly constant $[O_3]$.Agreement between model and measurement indicates that these rates are better known than is currently believed.

The experimental measurements constrain two aspects of Eq. 1. First, the precision of the measurements allows us to define a criterion of calculated-observed agreement that restricts the ratio of the rates of reactions in the model. However, this does not constrain the absolute rates of these reactions; multiplying all of them by a constant would give equally good agreement. Second, the combination of the relative rates, the absolute uncertainty in the measurements, and the accuracy of one rate constant sets limits on the constant by which we may multiply all of the rates.

We define a dimensionless standard error (DSE) as the root-mean-square difference between the model and the 6752 individual measurements of OH/HO_2 where the measurements are weighted by the inverse square of the experimental precision. Doubling of the DSE is comparable to 2σ confidence intervals (1σ intervals are taken as half the 2σ intervals). Using this standard, uncertainties (with respect to the precision but not the accuracy of the measurements) in the rates are derived by varying each rate *individually*. These limits indicate how much the *ratio* of the rates for the different reactions may change without compromising the overall agreement between the calculation and the measurements. The results appear in Table 1 under the heading Relative Uncertainty. The table should be interpreted as follows: if all five rate constants are held at the ratio defined by JPL'92 except k_1, then this rate constant is only consistent (to within 1σ) with the data if it is 0.96–1.06 times the JPL'92 value. Similarly, the data are consistent with Eq. 1 if the rate of HO_2+ClO is 0–1.75 times the JPL'92 recommendation.

Table 1. HO_x Reactions and Uncertainties

Reaction	Rate ($\times10^{-13}$)* cm^3/mol-s	Uncertainty (210 K)*†	Relative Uncertainty†‡	Absolute Uncertainty†‡
R_1	$16\times e^{-940/T}$	0.5–2.0	0.96–1.06	0.71–1.36
R_2	$0.11\times e^{-500/T}$	0.38–1.5	0.8–1.15	0.59–1.47
R_6	$3.7\times e^{250/T}$	0.75–1.34	0.88–1.15	0.75–1.34
R_{3a}	$4.8\times e^{700/T}$	0.26–2.0	0–1.75	0.26–2.0
R_{3b}	$62\times e^{500/T}$	0.17–6.1	0×1.75	0.17–2.2

*DeMore et al. [1992]; †All uncertainties are 1σ and multiplicative; ‡This work

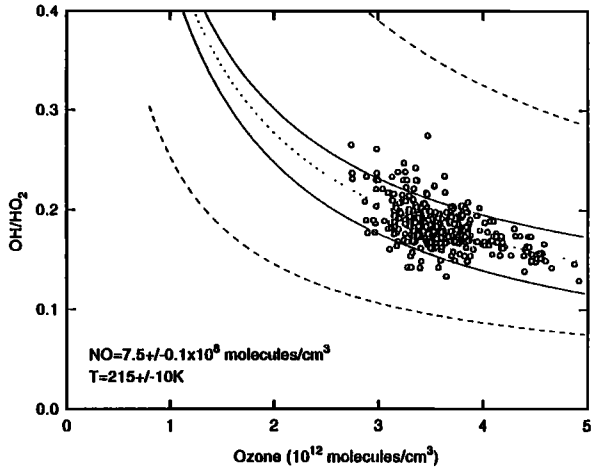

Figure 2. Measured (o) and modeled OH/HO_2 vs. simultaneously measured $[O_3]$. The dotted line (...) is a calculation of the ratio using JPL'92 rates and measurements of O_3, NO, ClO, and BrO. Dashed lines (—) are calculations at JPL'92 1σ error limits for the rate of OH+O_3. Solid lines are the same for HO_2+O_3.

The accuracy of the rates can be constrained as well. Consider the case where the numerator in Eq. 1 is dominated by k_6[NO], and the denominator by $k_1[O_3]$. (In the atmosphere, this is not unusual.) If we then solve for k_1

$$k_1 = [HO_2]/[OH] \times (C \times k_6') \times [NO]/[O_3], \qquad (2)$$

the absolute uncertainty in k_1 can be calculated from the accuracy of the right side of Eq. 2 and the relative uncertainty in k_1. In Eq. 2 we take into account that the measured HO_2 concentrations depend on the ratio of the rates for R_6 and R_7. Assuming k_7 is exact at the JPL'92 value, the effect of changes in k_6 can be expressed as a multiplicative constant, C, where C=1+.25(1-k_6'/k_6) and $k_6'\equiv$ a new value of k_6. For example, if k_6' were

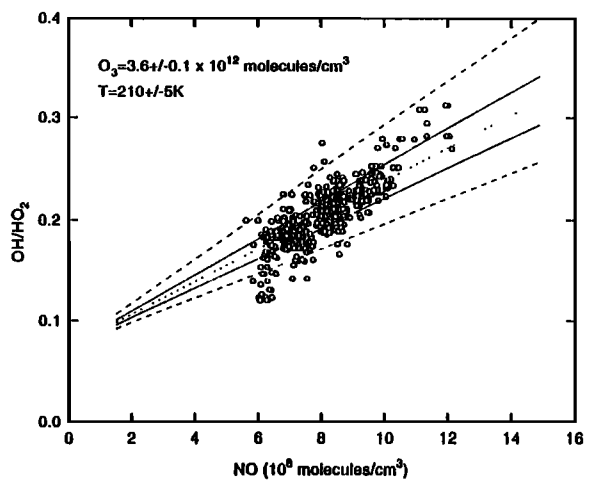

Figure 3. Measured (o), and modeled OH/HO_2 vs. simultaneously measured [NO]. The dotted line (...) is as in Figure 2. Dashed lines (—) are calculations at JPL'92 1σ error limits for the rate of HO_2 + NO. Solid lines correspond to 1σ error in the measured NO.

determined to be 25% faster than k_6, the inferred $[HO_2]$ would decrease by 6.25%. C and k_6 are anticorrelated; thus the product $C \times k_6$ is less uncertain than either term individually.

Assuming the accuracies of the individual terms on the right hand side of Eq. 2 $[HO_2]/[OH]$ (±0.13), $[C \times k_6]$ (-0.20, +0.23), [NO] (±0.1), and $[O_3]$ (±0.02), add in quadrature, the accuracy in k_1 (converted to a multiplicative factor) is 0.74–1.28 times the relative uncertainty in k_1 (0.96–1.06). The agreement between Eq. 1 and the measurements is not degraded if we multiply *all* the reaction rates by a constant. The same factor of 0.74–1.28 times the relative uncertainty is therefore the accuracy derived for all of the rates. Table 1 shows the smaller of the absolute uncertainty derived here and that given by JPL'92 as our best estimate of the accuracy of each rate. These are an improvement in the uncertainties of the reactions OH and HO_2 with O_3 and of HO_2 with BrO. The latter constraint is particularly important. The rate of HO_2 + BrO is thought to be uncertain to a factor of 6. Also, BrO in the calculations is uncertain to a factor of 1.5. We assume the modeled BrO is exact and determine the product of the rate constant and the BrO concentration to be not more than 2.2 times our initial input.

Another possible source of error in the model of the HO_x partitioning is "missing chemistry." If a reaction were found that could compete with the reactions cycling OH and HO_2, then the conclusions we draw about the uncertainty of each rate would require reevaluation. Because the measurements demonstrate that reactions that are a net source or sink of HO_x do not proceed fast enough to affect the ratio, we need only consider the effect of reactions interconverting OH and HO_2. To be significant, the reaction must alter the modeled OH/HO_2 by at least 10%. Assuming a rate constant of 1×10^{-10} cm^3/mol-s, as fast as any known reaction of HO_2, changing the ratio by 10% requires 6×10^6 –1.6×10^7 mol/cm^3 (~3–8 ppt). The ratio also might be affected by a reaction transforming OH to HO_2. Assuming a rate constant of 1×10^{-10} cm^3/mol-s, 3×10^7–1.2×10^8 mol/cm^3 (15–60 ppt) is needed to affect the ratio at the 10% level.

Conclusions

In situ measurements of the ratio of OH to HO_2 obtained simultaneously with NO, O_3, ClO, and BrO are reproduced to remarkable accuracy by current models. Because [OH] is nearly independent of the chemical constituents in the stratosphere [*Wennberg et al.*, 1994a] an understanding of this ratio is equivalent to understanding the absolute abundance of HO_2. The model-measurement agreement shows:

1) The two reactions in the ozone-destroying HO_x catalytic cycle are accurately described by the JPL'92 rate expressions. The uncertainty in the rate of the HO_2 + O_3 reaction, the rate limiting step in the catalytic removal of ozone by HO_x, is reduced from a factor of 2.6 to a factor of 1.6 at 210 K. The product of the BrO concentration and the rate of the HO_2 + BrO is more certain by a factor of 3. These results translate directly into increased confidence in modeling catalytic ozone loss rates in the lower stratosphere.

2) The accuracy of descriptions of the abundance of HO_2 is set by our knowledge of the ratio of the rates of $R_{1\text{-}6}$ and R_8 (and by our ability to model the concentration of OH) and not their absolute values. The relative rates of R_1, R_2, and R_6 are now constrained to better than ±20% at 205–225K.

3) The sensitivity of the ratio of OH to HO_2 in the lower stratosphere to variations in NO is accurately (+10%,-12%) described by R_6 as parameterized in current models. Thus, the impact of potential changes in NO_x concentration on the radical (HO_2) responsible for most of the ozone loss rate in the lower stratosphere is shown to be quantitatively correct by direct measurements in the atmosphere. This reaction is the centerpiece of the NO_x/HO_x coupling, and the accuracy of it is a lower limit on the uncertainty in the evaluation of the impact of High Speed Civil Transports, large volcanic eruptions, or any other perturbation to NO_x in the lower stratosphere.

4) The potential effect of "missing chemistry" on the partitioning of HO_x radicals is limited. Changes of more than 10% to OH/HO_2 require in excess of 3 ppt of a radical reacting with HO_2 with a bimolecular rate constant for the reaction of 1×10^{-10} cm^3/mol-s or more than 15 ppt of a radical reacting with OH, with a rate constant of 1×10^{-10} cm^3/mol-s.

Finally, the SPADE experiments provide constraints on the reactions that dominate HO_x partitioning in the mid-latitude stratosphere near 20 km. At lower altitudes or latitudes, reactions of OH with CO and with CH_4 are much more important. In the polar regions during winter, reactions of ClO and BrO will be much more important. In both regimes, it may not be possible to neglect net HO_x production and loss. Experiments in these environs are clearly needed to provide constraints on the HO_x chemistry and especially on the HO_2 abundance to test the accuracy of models of the odd-oxygen production and loss rates in the lower stratosphere.

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